Overview of passive samplers for assessing contaminants in water

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Passive samplers – What are they?

Abiotic device used to monitor for a chemical(s) in an environmental medium

- Has little or no moving parts
- Doesn't require power to operate
- Samples over prolonged durations (hours to days to months)

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Benefits of Passive Samplers

Concentrate large volumes of water (10s to 100s L) resulting in increased sensitivity and lower detection limits than may be possible with a grab sample of 1 – 2 L of water.

Provide time-weighted average concentrations which are a fundamental part of ecological risk assessment processes for chemical stressors.

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Benefits of Passive Samplers

Selectively samples residues from the dissolved (readily bioavailable) phase – mimicking an organism's exposure.

Detect episodic changes in environmental contaminant concentrations that are often missed with grab samples.

- The maximum concentration and the timing of the event is unknown, but presence of the chemical is usually determined

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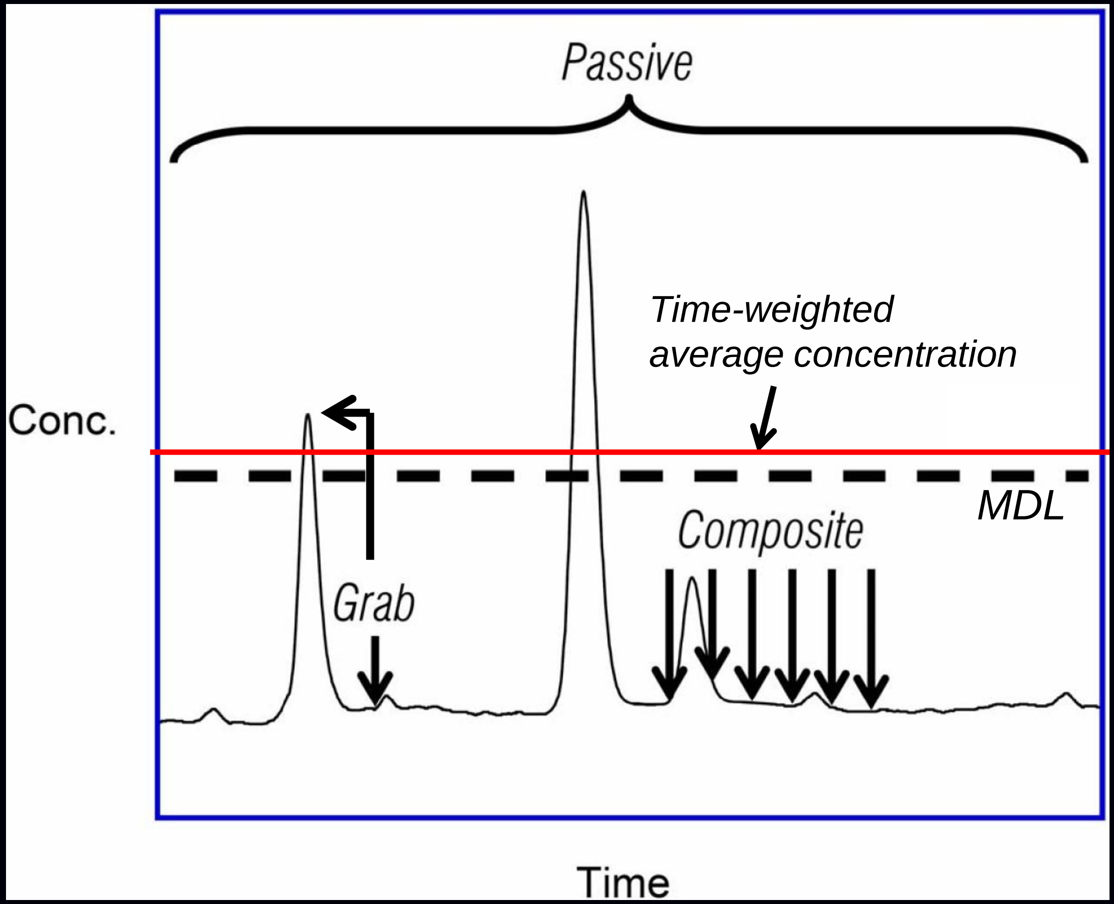
Grab vs. Composite vs. Passive Sampling Techniques



Grab / Discrete Sample

- Small vol (1-2 L)
- Single point in time
- Detection based on conc. and method detection limit

Composite sample

- Larger vol. over time
- Labor intensive
- Improved odds of detecting low conc.

Passive / Integrative sample

- Large vol. sampled (10s-100s L)
- Time-weighted average conc.

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Comparison to Biota Sampling

Passive samplers don’t move.

Metabolism/excretion of sampled chemicals is not an issue.

No need to analyze multiple tissues to obtain the full picture of exposure to dissolve phase chemical

- Does not assess exposure to particle-sorbed chemical via e.g., feeding

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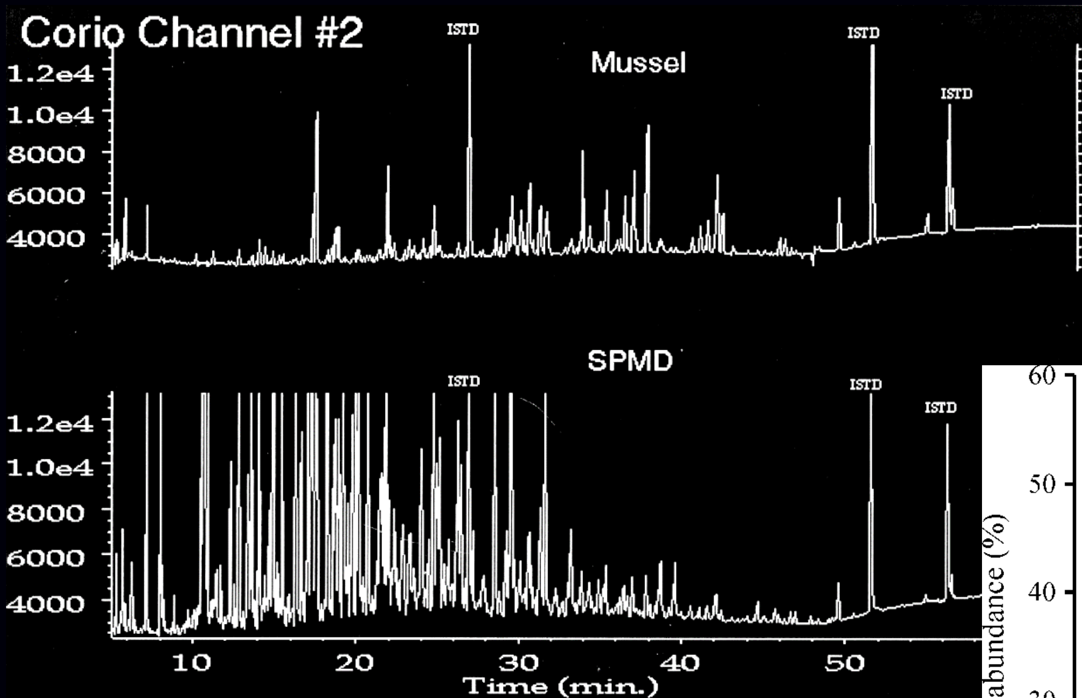
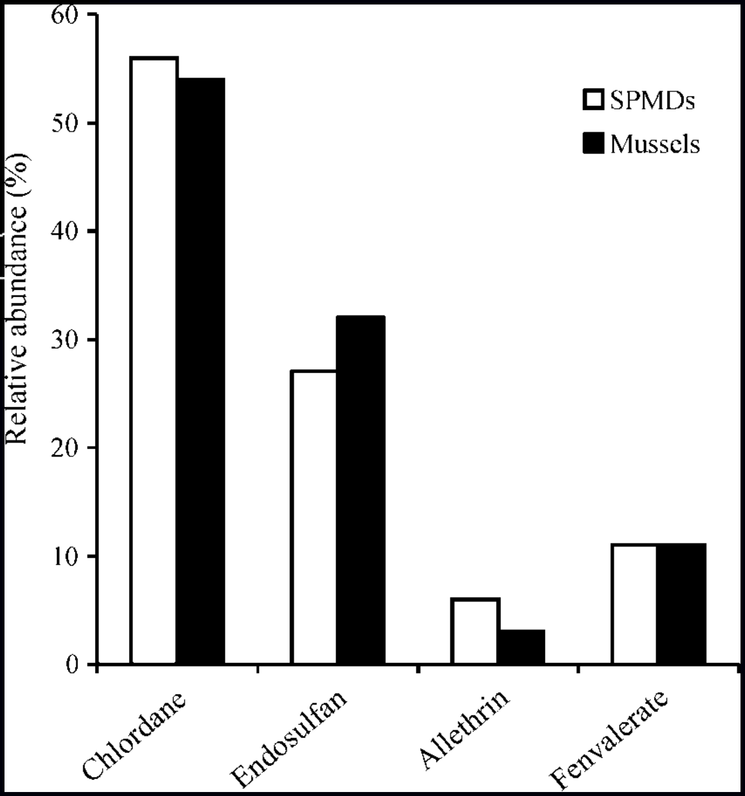
Passive Sampler and Biota Comparison



Sampling of chlorinated organics



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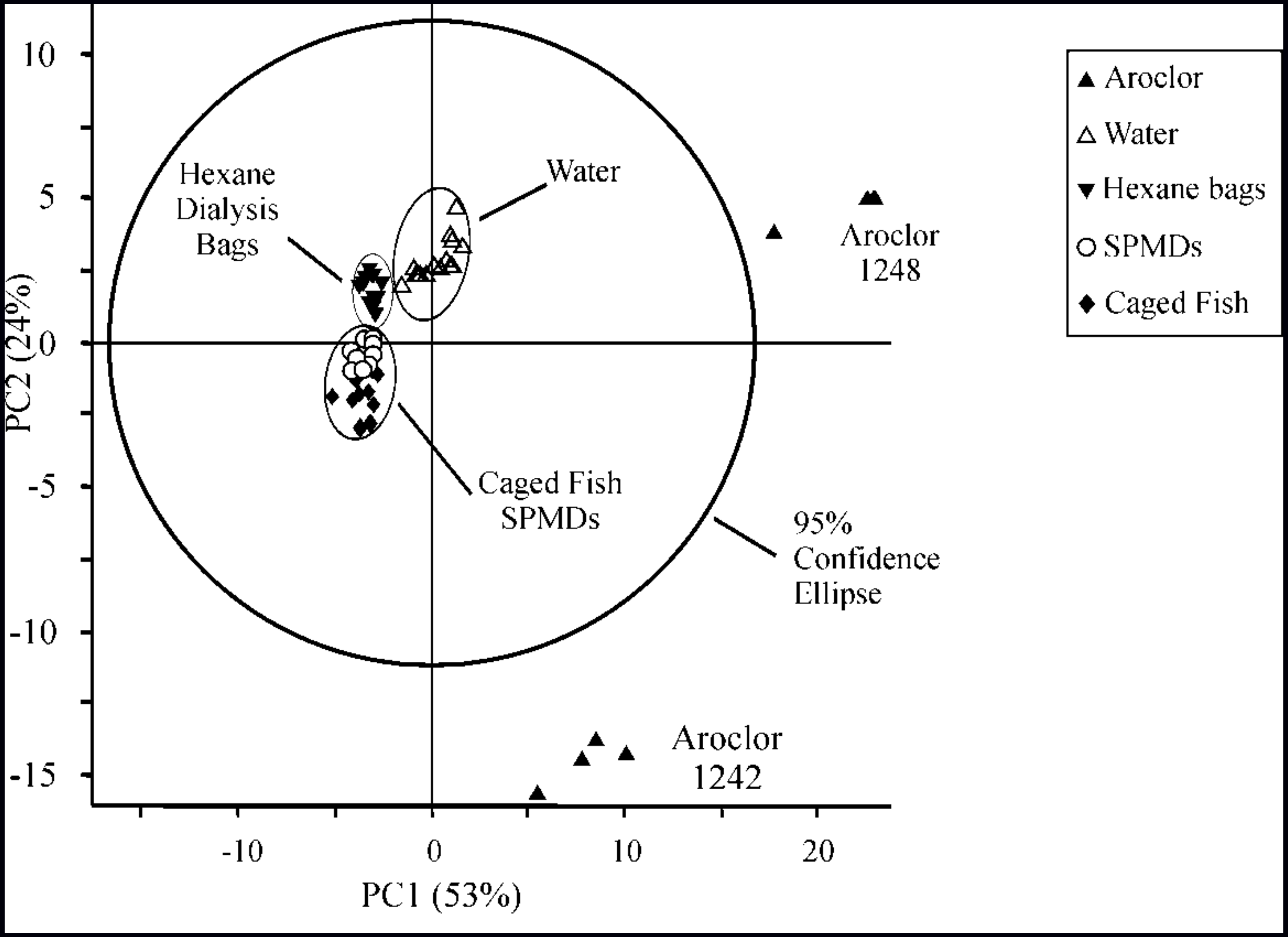
Passive Sampler and Biota Comparison



Comparison of Caged Fish, SPMDs, and Water for PCBs

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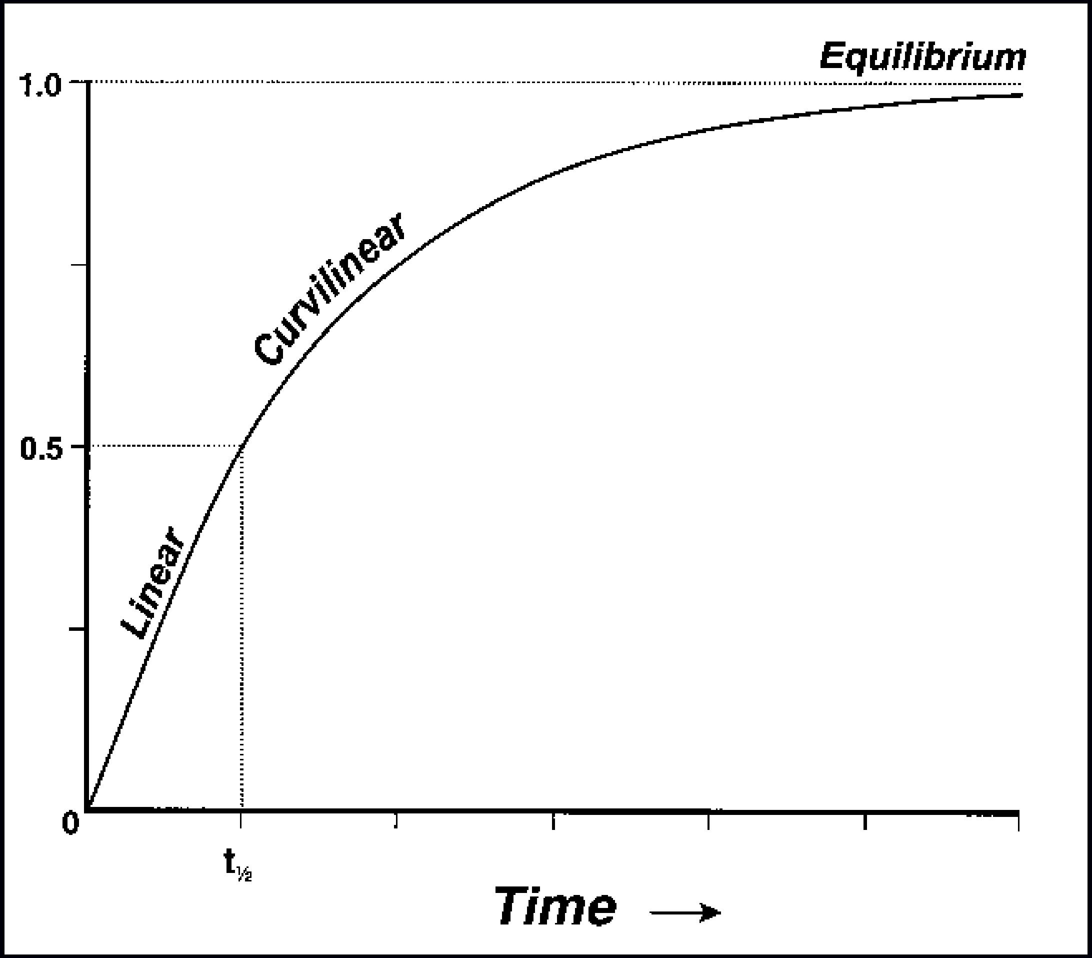
Accumulation of Chemicals by Passive Samplers



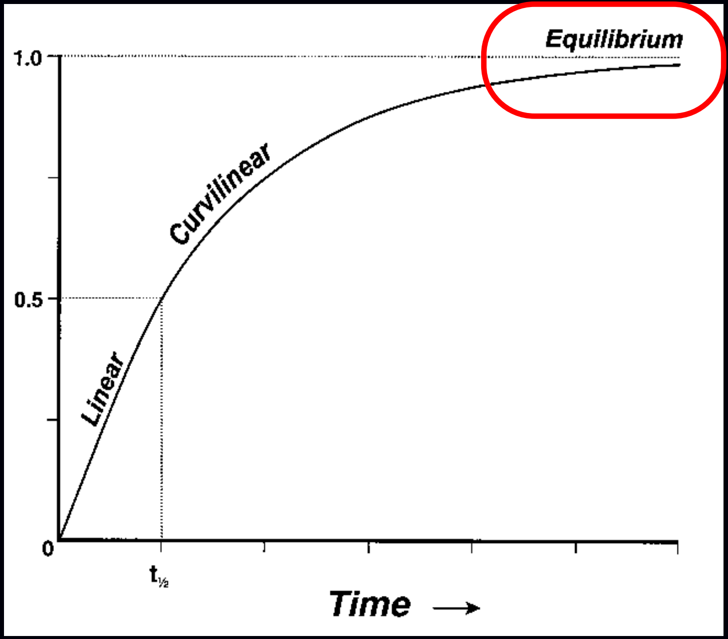
Uptake follows first-order kinetics

Uptake and elimination constants are independent of chemical concentration

General Types of Passive Samplers

Equilibrium samplers –

- Chemical reaches equilibrium partitioning condition with sampler media relatively quickly; e.g. lower sampler/water partition coefficient
- shorter exposure times (days to weeks)
- low capacity
- data most representative of the latter stages of the deployment
- groundwater, sediment pore water, air, some surface water
- Solid phase microextraction (SPME), polymers on glass, diffusion samplers



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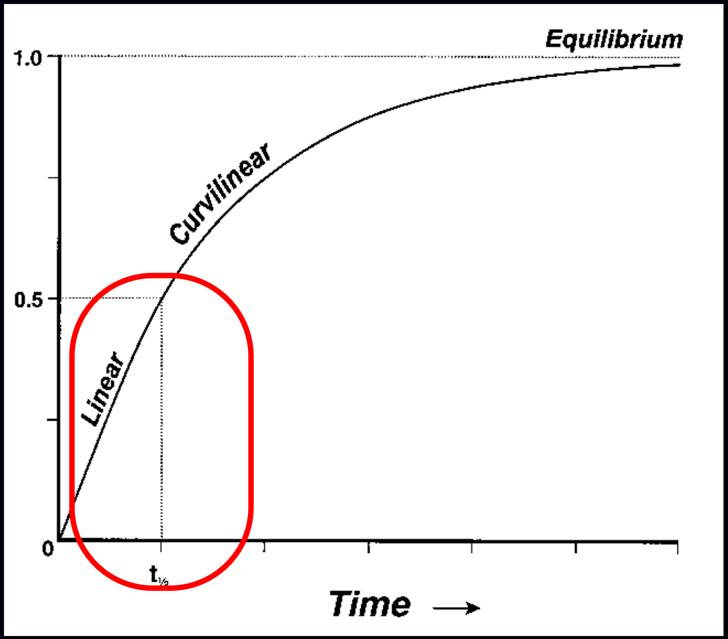
General Types of Passive Samplers

Integrative samplers –

- Chemical has greater sampler/water partition coefficient
- Long exposure times (weeks to months) – generally 1-2 months
- Short deployments = smaller volumes sampled
- Long deployments = risk of reduction of sampling rates due to biofilm buildup and change from integrative to equilibrium sampler
- Can act as Integrative and Equilibrium sampler at same time



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General Types of Passive Samplers

Integrative samplers –

- high capacity
- provides Time-Weighted Average concentrations over whole deployment
- surface water, air, some groundwater
- Examples:
  - SPMDs
  - POCIS
  - Chemcatcher
  - PE or Silicone strips

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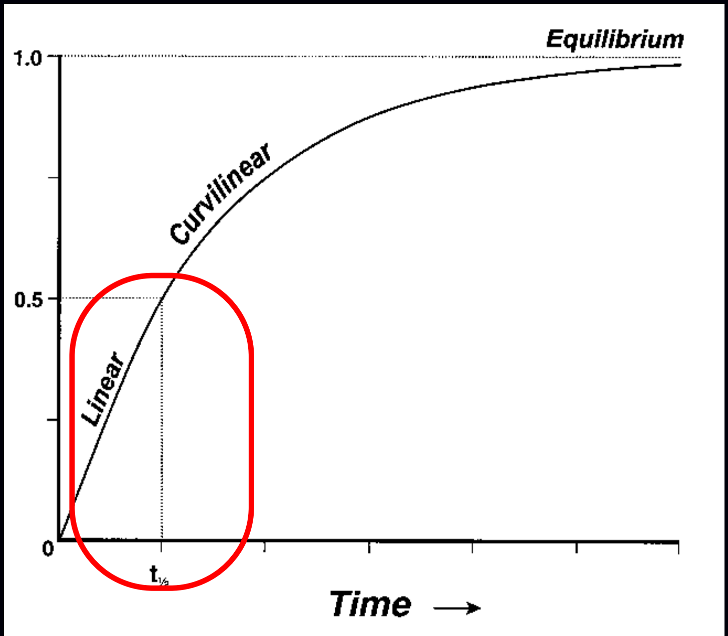
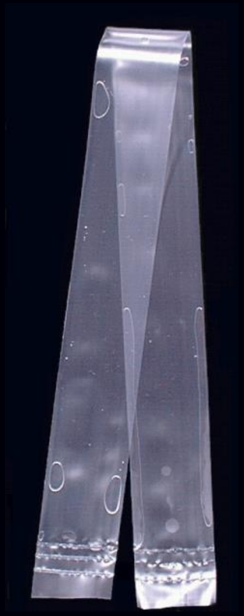


Widely used samplers for organic chemicals

- Semipermeable Membrane Device (SPMD)
  - Lipid soluble chemicals (log K_{ow} > 3)
  - Triolein (lipid) filled polyethylene (LDPE) tube
  - Useful for both water and air sampling



SPMD

- Polar Organic Chemical Integrative Sampler (POCIS)
  - Water soluble chemicals (log K_{ow} < 4)
  - Solid phase sorbents held between PES membranes
  - Sorbents and membranes can be changed for specific applications

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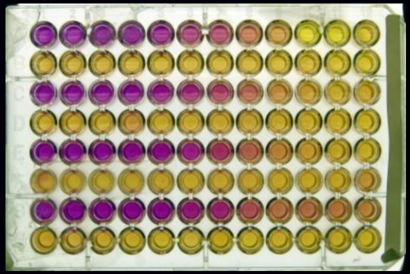
Chemicals commonly sampled by SPMDs/POCIS

- **Legacy / regulated contaminants (SPMDs)**
  - Polycyclic aromatic hydrocarbons (PAHs)
  - Polychlorinated biphenyls (PCBs)
  - Polybrominated diphenyl ethers (PBDEs)
  - Chlorinated pesticides (DDT, chlordanes, etc)
  - Dioxins and Furans

- **Emerging Contaminants (POCIS)**
  - Fragrances
  - Hormones
  - Pharmaceuticals / Illicit Drugs
  - Current-use pesticides
  - Antimicrobials (triclosan)

- **Bioindicator Tests (SPMDs and POCIS)**
  - In vivo and in vitro assays



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Barriers to Chemical Uptake

Uptake (and loss) rates are control by chemical diffusion across multiple barriers

The thicker these barriers are, the slower diffusion across the barrier

Diffusion across these barriers is dependent on the physicochemcial properties of the chemical

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Performance Reference Compounds (PRCs)

Increasing the Accuracy of your Data

Performance Reference Compounds (PRCs)

PRCs are added to SPMDs during construction to account for the effect of environmental conditions on sampling

- Non-interfering (analytically)
- Not present in the environment
- Cover a range of fugacities (ability to leave the SPMD)
- Preferably compatible with the target analytical method

Common to use multiple PRCs in ensure at least one has usable data

Caution -

PRCs should not be added to samplers which will be used for bioindicator/toxicity determinations.

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PRC Approach: Isotropic Exchange

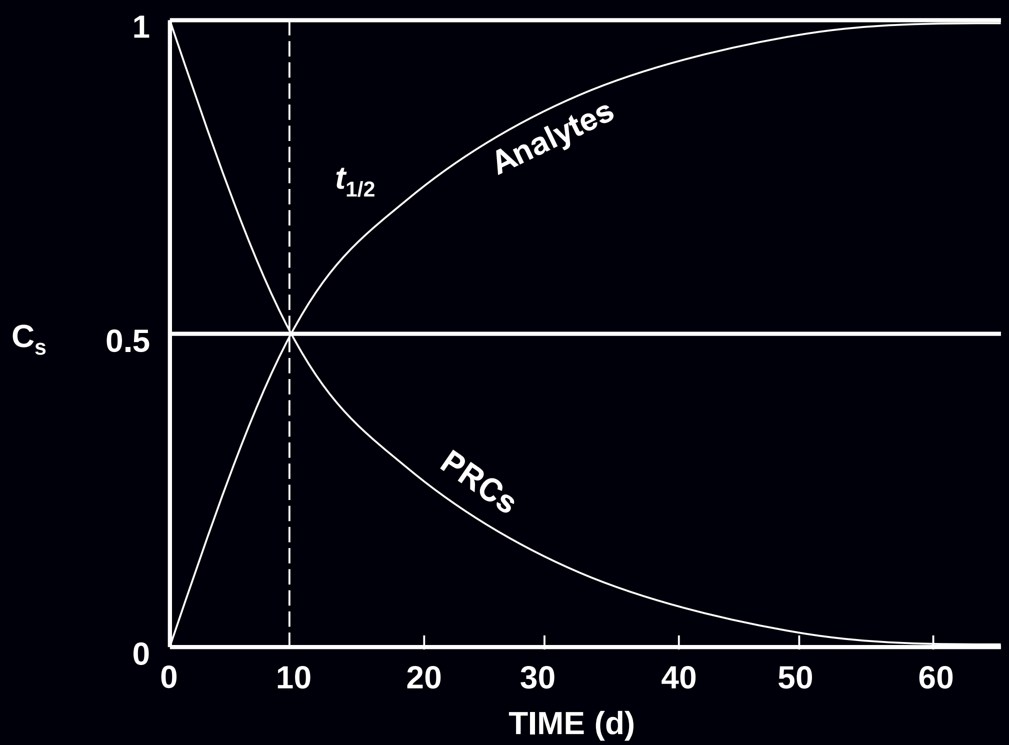

Figure 1. Illustration of isotropic exchange kinetics.

Uptake Rate ≅ Loss Rate

$(k_u \cong k_e)$

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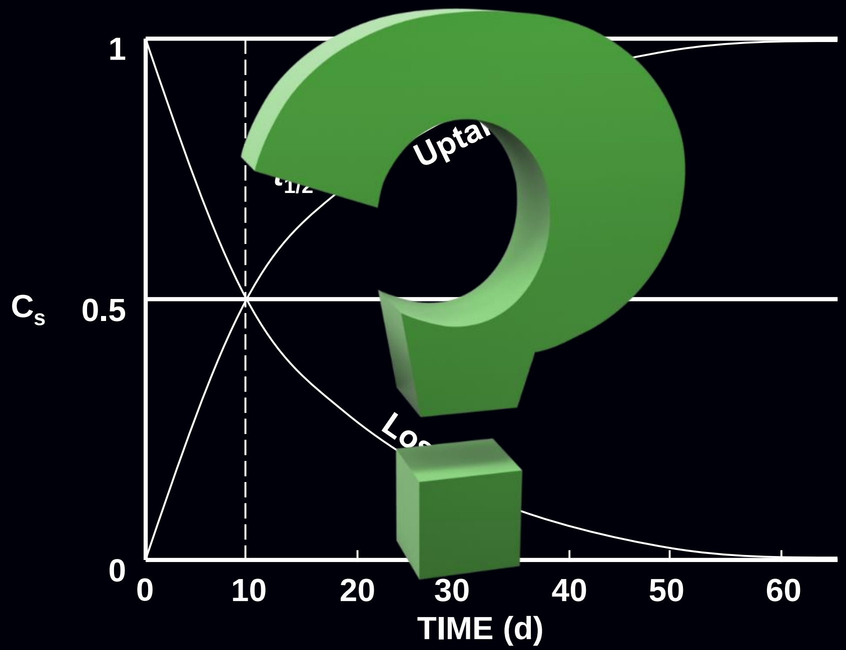
PRC Approach

Why use PRCs?

- Sampling rate (R_s) can increase 10-fold due to changes in water velocity (or air velocity, for air sampling)
- R_s can increase 4-fold due to temperature changes
- R_s can decrease 3 or 4-fold due to biofouling
- Photolysis of selected chemical classes (especially PAHs) can occur

Performance Reference Compounds (PRCs) for POCIS ?



PRC approach is limited to chemicals of similar structure and generally for chemicals with low log K_{ow}s.

Reason - Chemical release from a polymeric sorbent (such as Oasis HLB) is not an isotropic process

Most successes have been for pesticides using DIA-d5

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Study Design

Things to think about when planning a study using passive samplers

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Study Design

1) Are passive samplers the best option to meet study goals?
2) What type of sampler is appropriate for my needs and where can I procure them?
3) Does the analytical lab have experience with passive samplers?
4) What methods/instrumentation will be used and are they compatible with the passive samplers and PRCs used?
5) How low do you need to measure and how many samplers do you need?
6) What Quality Control (QC) is required?

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Field Considerations

1) Must remain submerged at all times

2) Keep from getting buried in sediment

3) If photosensitive chemicals are targeted, protect from light (add a photolysis marker as part of PRC mix)

4) Be prepared for flooding and/or floating debris

5) Beware of other people - #1 cause of failed field work

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Quality Control and Lab Work

What is needed

and what should I expect?

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Quality Control

Blanks –

Blanks are essential to confirm measured levels of contaminants from field deployed samplers that were not introduced as "background" from the sampler materials, laboratory processing, storage, shipping, or field handling.

SPMDs readily sample air therefore *Field* and *Laboratory* Blanks are necessary.

No amount of precaution can remove all traces of background contamination.

Quality Control

Recommended Frequency –

Blanks at all sites is best, but can be very expensive.

10 – 20% of samples for QC is a common practice

Alternative option – use a “cumulative field blank” which is a blank opened at multiple sites.

Quality Control

Analyte Recovery Samples (Spikes) –

Passive sampler spiked with target chemicals should accompany every study set to the extent possible

- especially important for volatile chemicals and non-standard chemicals

- can be difficult to accomplish as the lab extracting the samplers may not be the same as the lab performing the analyses (spiking solutions may not be available)

- Some recovery data can be found in the literature

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Considerations when choosing a laboratory

Many laboratories do not have experience working with passive samplers, therefore initial contact is *CRITICAL*.

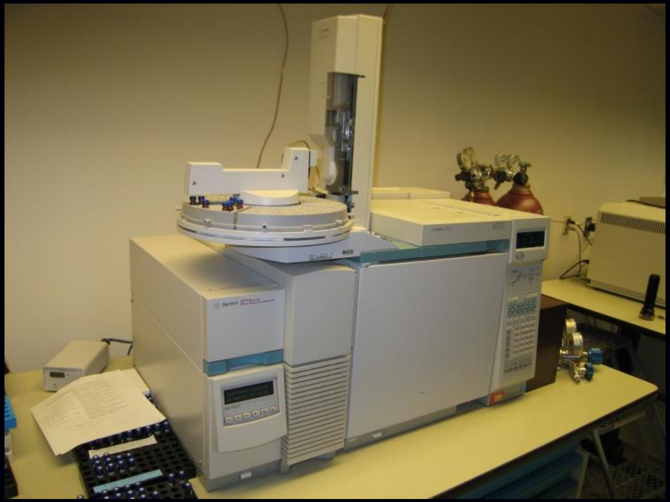
Issues to be discussed:

- What internal standards / surrogates do they use (may be same as PRCs added to samplers which may limit certain PRC use)?

- Can they analyze the PRCs as part of their methods and at what concentrations?

- How will the data be reported?

  ng/sample needed for calculations.



Data, Applications, and What Does It All Mean

Will passive samplers provide me with the data I need to satisfy the project's goals?

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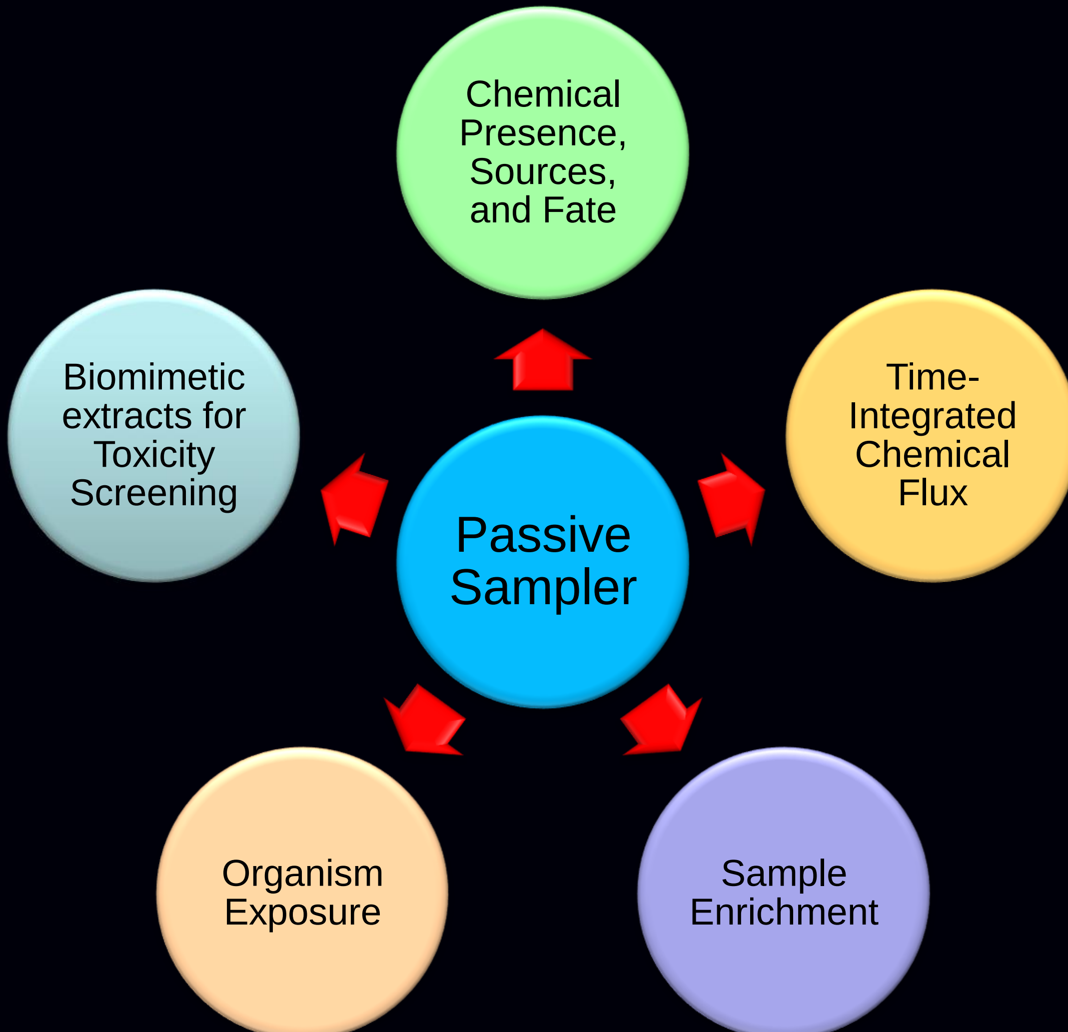
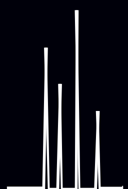
Applications of Passive Samplers

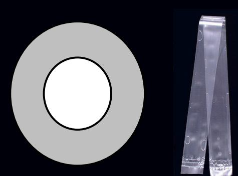


Estimating Water Concentrations

GOAL – Accurate estimation of time-weighted average water concentrations



Chemical Analysis



ng / sampler

ng / L

What's Needed? – Understanding of the fundamentals of chemical transport into the sampler, quality of available information, uncertainties, and misinterpretations of the data.

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Estimating TWA Water Concentrations From SPMD and POCIS Data

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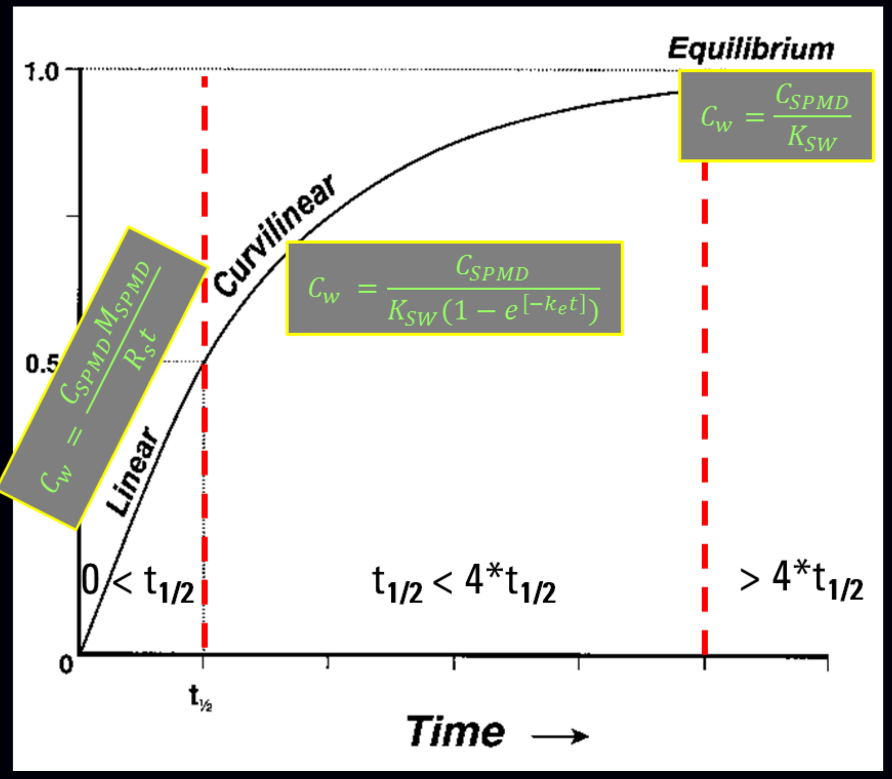
Uptake Follows First-Order Kinetics

Without the use of PRCs, C_w is calculated using uptake models specific to the position on the uptake curve. This is chemical-specific and only can be used for chemicals which have experimentally-determined R_s values.

$t_{1/2}$ is calculated to determine the phase in which sample is occurring

$$t_{1/2} = \frac{-\ln 0.5 K_{SW} V_{SPMD}}{R_s}$$



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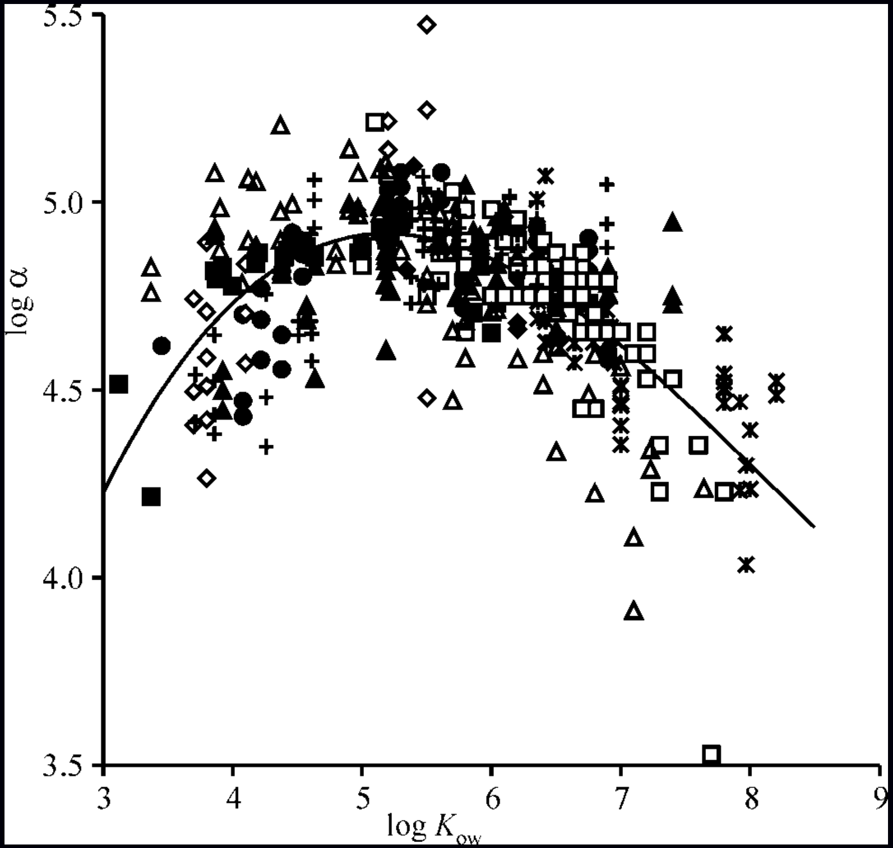
PRC-Based Calculation overview for SPMDs

An Empirical Uptake Rate Model was created to describe the entire uptake curve using experimental calibration data based on PRC loss, chemical uptake, and chemical K_{ow}s.

$\alpha_{(i/PRC)}$ = the compound-specific effect on the sampling rate

K_{ow} = Chemical's octanol-water partition coefficient



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Data Calculations for SPMDs

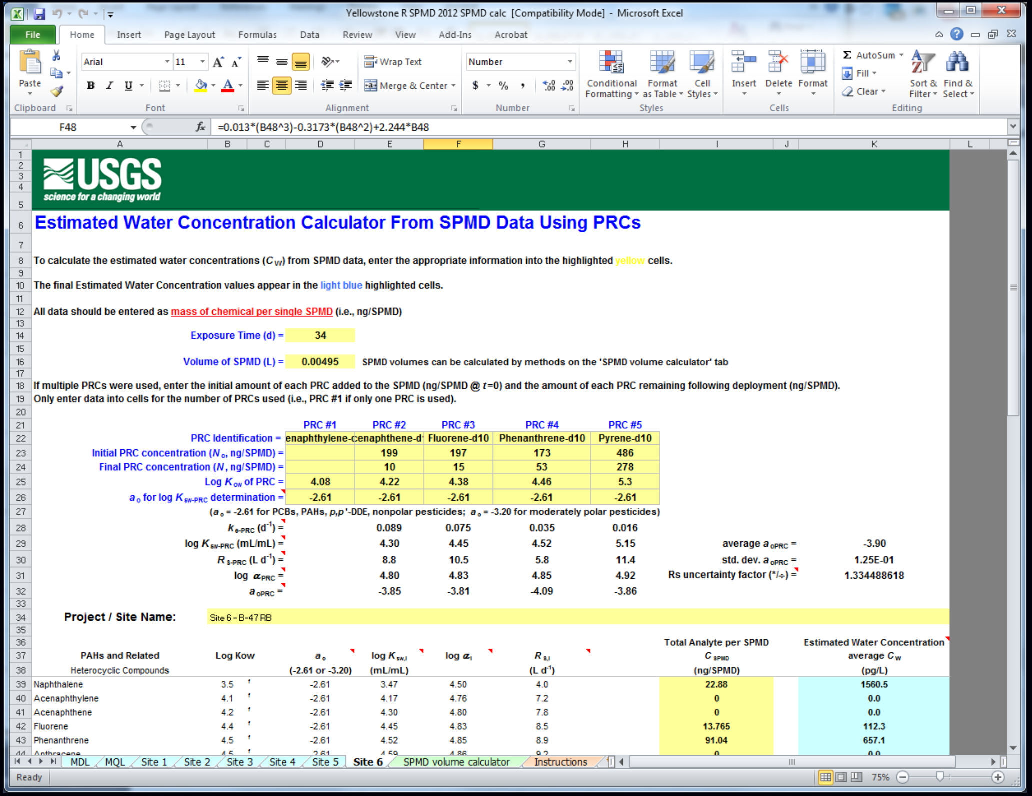
Uptake models are be complex

Customizable spreadsheets are available to download to aid in SPMD calculations

Two versions available:

1) If PRCs were used – can be modified to calculate water concentration for nearly any chemical (version 5.2)

2) If no PRCs were used – limited to chemicals for which sampling rates have been experimentally determined (version 4.1)



https://www.usgs.gov/cerc/passivesampling

Calculating Water Concentrations from POCIS

For many chemicals, linear uptake has been shown to continue for 28 to 56 days.

Highly polar chemicals with log K_{ow}s approaching 0 can reach the curvilinear phase within a few weeks, however, uptake for these types of chemicals have not been thoroughly modelled.

Linear Phase (assumed and used for all POCIS calculations) –

$$C_w = \frac{N_{POCIS}}{R_s t}$$

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POCIS sampling rates (R_s)

$$C_w = \frac{N_{POCIS}}{R_s t}$$

R_s values are experimentally determined.

A method to theoretically estimate R_s values exists, but this method tends to underestimate the R_s potentially overestimating C_w

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POCIS sampling rates (R_s)

Sampling rates have been experimentally determined for approximately 350 chemicals

Pesticides (182)

Waste Indicator Chemicals (17)

Illicit Drugs (9)

Industrial Chemicals (24)

Pharmaceuticals (87)

Hormones (16)

Microcystins

Perfluorinated Surfactants (12)

Several chemicals have been tested by multiple methods.

R_s values generally range from 0.1 to 0.4 L/d

Recommendations for selecting POCIS R_s values

Review articles covering these topics –

Harman et al. *Environ Toxicol Chem* 31 (2012) 2724-2738

Booij and Chen *Environ Toxicol Chem* 37 (2018) 1786-1798

Carefully read and understand the conditions from which R_s were derived.

- Are the exposure conditions and time similar to your study?
- Is the same type of POCIS being used?
- Is the R_s based on the sorbent only or the whole POCIS?

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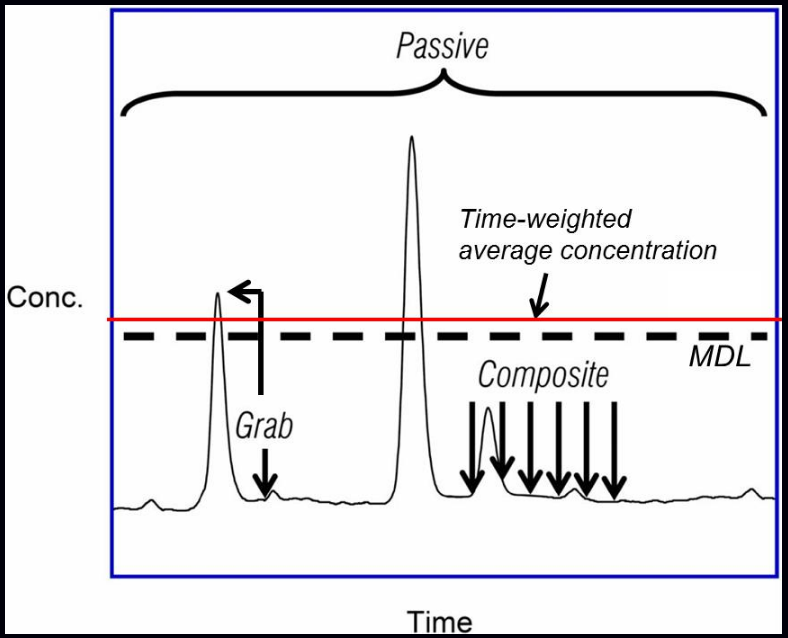
Limitations of using passive samplers

Integrative samplers are designed for long-term sampling periods. Little benefit over grab sampling for durations less than a few days.

Although episodic events (storm runoff, spills, etc.) can be captured, its impossible to know maximum concentration or when event occurred.

Estimation of water concentrations may not be possible for all chemicals of interest.



Cautions when comparing data

Beware of dangers when comparing passive sampler data to traditional grab sampling data.

Unless a rigorous grab sampling program (multiple samples) was used, there is no reason to expect a single data point will be representative of the average conditions measured by a passive sampler over weeks or months.

The different techniques should be considered complimentary, but not necessarily interchangeable.

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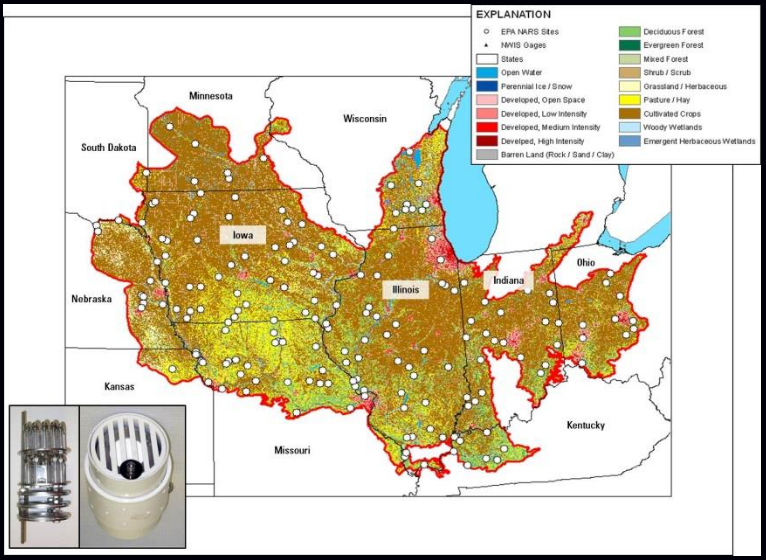
POCIS-Water Data Comparison

100 sites across 11 states were sampled for 20-50 days in 2013 and compared to weekly water samples as part of a NAWQA regional study.

Samples analyzed for 113 pesticides and 116 pesticide degradates.



Detection Frequency –

POCIS generally detected more chemicals than grab (median of 62 and 46)

Concentrations –

14 chemicals with high detection frequency in both sample types were compared

Good correlation in relative magnitude of concentrations between sites

Van Metre et al. Environmental Pollution 220 (2017) 431-440

Regulatory acceptance

Samplers as personal dosimeters (human health) for determining occupational exposure is widely accepted.

Use as an environmental monitoring tool is rapidly gaining acceptance.

- in US - often viewed as a research tool by federal agencies
- a few States have using passive samplers in TMDL and reconnaissance studies
- EU is conducting studies to determine the viability for regulatory use

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Regulatory acceptance – Examples

US Government –

- USGS using as part of NAWQA monitoring program
- USGS using in contaminant tracking studies in the Great Lakes
- USGS using SPMDs in PCB remediation studies
- EPA using in wastewater source tracking studies

Note – USGS and EPA studies are not regulatory

- DOI's NRDAR program using SPMDs in oil spill cases (Deepwater Horizon, multiple spills along the Yellowstone River)

Regulatory acceptance – Examples

State Government –

- State of WA Dept of Ecology – using SPMDs for monitoring and TMDL studies
- State of OR and State of VA have a history of using SPMDs for similar purposes
- State of PA Dept of Environmental Protection – using SPMDs/POCIS data for developing management plans for aquatic health and drinking water sources
- State of FL DEP – proposed using SPMD/POCIS to provide information on emerging contaminants in watersheds to become prepared for future regulations

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I’m sold, so where can I get some samplers?

Sources and Options

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Sources of SPMDs and POCIS

Commercial Vendor -

Environmental Sampling Technologies (EST)

St. Joseph, MO

Lab Manager – Jon Hoppe

816-232-8860

www.est-lab.com

SPMDs and POCIS

Research Collaborator -

USGS Columbia Environmental Research Center

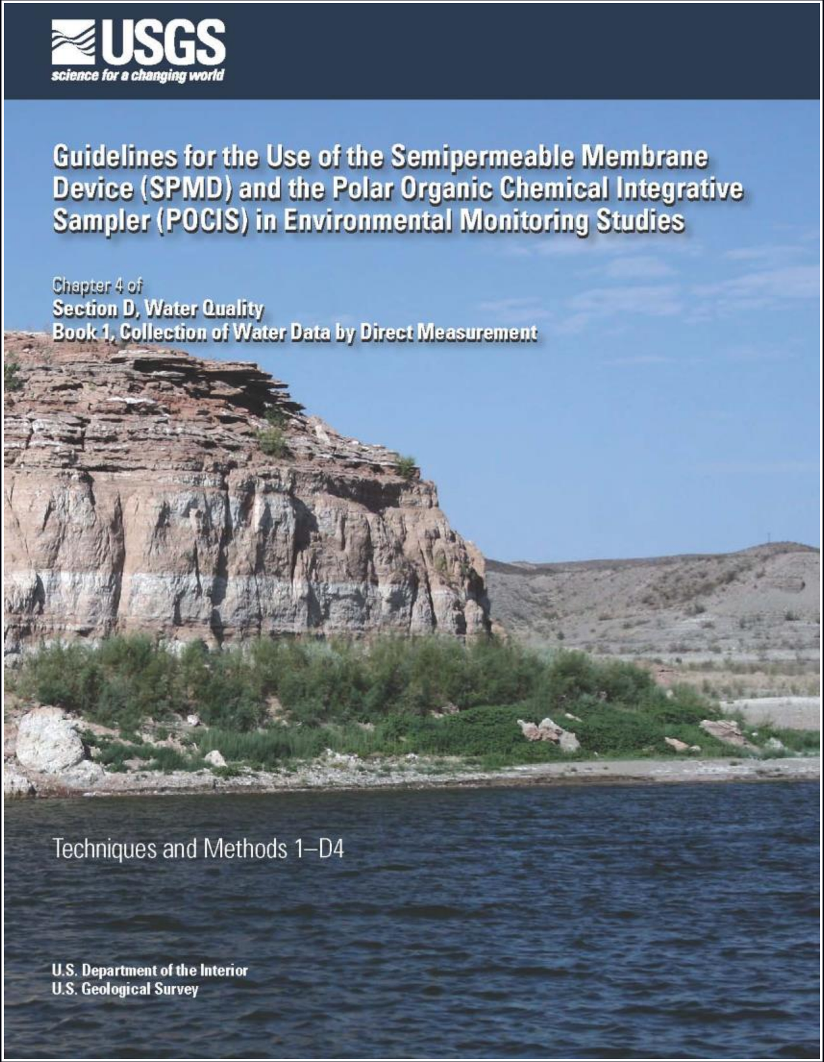
Columbia, MO

Branch Chief – David Alvarez

573-441-2970

dalvarez@usgs.gov

More information



- David Alvarez
  - dalvarez@usgs.gov
  - 573-441-2970
- SPMD/POCIS "How-To" Guide
  - Techniques and Methods Book 1, Section D, Chapter 4
  - http://pubs.usgs.gov/tm/tm1d4/
  - Covers topics of
    - Before heading to the field
    - In the field
    - Back at the lab
    - I have data, now what?

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